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Reactions of singlet oxygen with cyclohexylidene compounds

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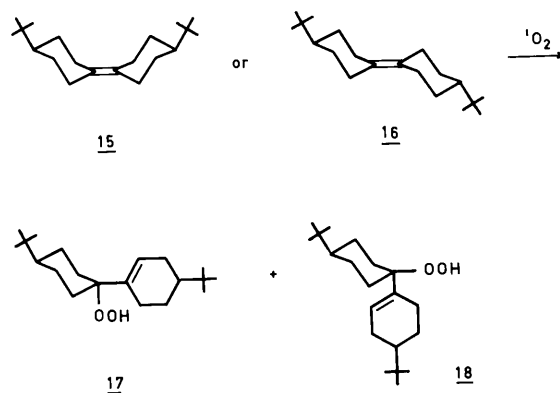
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S U M M A R Y

This thesis deals with the reactions of singlet oxygen with some olefins. In Chapter I some general aspects of singlet oxygen are discussed. The types of reactions that singlet oxygen can give are discussed as well as some of the conditions that the olefin has to fulfil.

In Chapter II the reactions from *syn*- and *anti*-4,4'-di-*tert*-butylcyclohexylidenecyclohexane 15 and 16 with singlet oxygen in the presence of sulphides are discussed. Each of these olefins gives a mixture of the allylic hydroperoxides 17 and 18 but it appeared, for example,

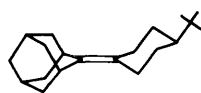


that in the photooxygenation of 15 in the presence of the additive dibenzylsulphide, instead of 17 and 18, 4-*tert*-butylcyclohexanone was formed. This result is caused by benzenesulphonic acid, which can be present as an intermediate in the photooxygenation of dibenzylsulphide and which induces rearrangement of the allylic hydroperoxide to 4-*tert*-butylcyclohexanone.

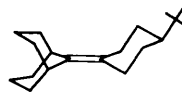
In Chapter III the results are reported from the reaction of 15 and 16 with singlet oxygen at different temperatures and also the results from the photooxygenation of two non-symmetrical olefins. It appeared that photooxygenating 15 that the lower the temperature, the

more 17 and the less 18 was formed. These results are, together with those from the reaction of 4-*tert*-butylcyclohexylideneadamantane 46 and 4-*tert*-butylcyclohexylidenebicyclo[3.3.1]nonane 47 with singlet oxygen,

Also the results for
fins are reported in this



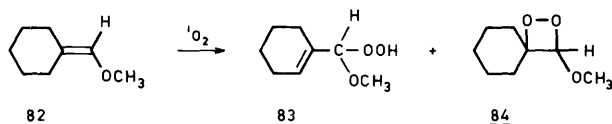
46



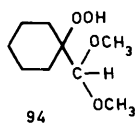
47

discussed and they can be understood best by assuming a zwitterion as an intermediate in the photooxygenation. To obtain proof for this assumption a substituted dodecahydrophenanthrene was required and the attempted synthesis of the requisite compound, together with the surprising synthetic result, are discussed in Chapter IV.

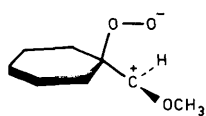
Chapter V deals with the reaction of some methoxymethylene compounds with singlet oxygen. It appeared, for example, that in the photooxygenation of methoxymethylenecyclohexane 82 besides the allylic hydroperoxide 83 also 1,2-dioxetane 84 can be formed and, moreover, that



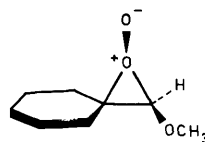
it is possible to influence the ratio allylic hydroperoxide dioxetane by changing the solvent and the temperature. When the photooxygenation of 82 was carried out in methanol as solvent, it appeared that besides 83 and 84 also a third product was formed to which structure 94 was assigned. One can understand the formation of 94 through trapping by methanol of intermediate 98 or intermediate 99.



94



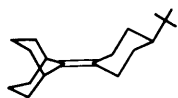
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99

results are, together with
hexylideneadamantane 46 and
adamantane 47 with singlet oxygen,

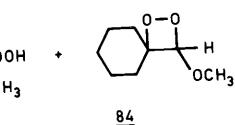
Also the results from the photooxygenation of some related ole-
fins are reported in this chapter.



47

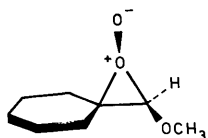
by assuming a zwitterion as
to obtain proof for this as-
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ing Chapter IV.

some methoxymethylene com-
pounds, for example, that in the pho-
tooxygenation of 82 besides the allylic hy-
droperoxide formed and, moreover, that



84

allylic hydroperoxide dioxetane
intermediate. When the photooxygenation
was carried out, it appeared that besides
the hydroperoxide to which structure 94 was as-
signed, a dioxetane of 94 through trapping by
the reagent 99.



99